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Comparative Studies on Mo–Cr–N and Al–Cr–N Coatings Obtained by PVD Dual Magnetron Sputtering

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Recently, several studies have shown that the addition of a secondary element likes Al, Si, etc. to nitride and carbide binary systems such as Ti–N and Cr–N improved their structural and mechanical properties and also their thermal stability. In this study, we realized a comparison between the effects of aluminium or molybdenum addition on the properties of the Cr–N system. The (Cr,Al)N and (Cr,Mo)N films were deposited by RF dual magnetron sputtering. To control the aluminium and molybdenum contents in (Cr,Al)N and in (Cr,Mo)N films, respectively, we modified the Cr, Al and Mo target bias. The structural, morphological and composition analyses of the deposited films were carried out using X-ray diffraction (XRD) and SEM equipped with an energy dispersive spectroscopy (EDS) microanalysis. The variation of the residual stresses with the Al and Mo contents has been studied using the Newton's rings method. The obtained Al contents in (Cr,Al)N deposited films varied between 0 and 51 at.% while the Mo contents in (Cr,Mo)N layers varied between 0 and 42 at.%. A morphological change from amorphous to columnar films has been observed with the addition of Al in the case of (Cr,Al)N coatings, while all the (Cr,Mo)N films presented a columnar structure. The residual stresses of the (Cr,Mo)N coatings are higher than the (Cr,Al)N ones but they exhibited a similar behaviour for both coatings.

Introduction

CrN coatings deposited by PVD methods are commonly used in metallic machining because of their high hardness and wear resistance.^[1] In addition, the Cr–N system has a high oxidation resistance up to 700 °C.^[2] Recently, several studies showed that the addition of aluminium to the Cr–N system increased its oxidation resistance up to 900 °C.^[3] On

the other hand, it has been shown that the development of ternary systems by adding a third element to binary ones permitted main results. Indeed, the addition of Mo,^[4] Si^[5] and C^[6] to the Cr–N system improved significantly its mechanical and tribological properties. The formation of solid solution by the substitution of the Cr and N atoms by these elements allowed the formation of new systems with higher mechanical and tribological properties than the CrN coatings' ones. In this study, (Cr,Al)N and (Cr,Mo)N coatings were deposited by RF dual magnetron sputtering in order to compare the effect of Al and Mo as the additive elements on the Cr–N system properties such as its composition, structure, morphology, stresses, etc.

Experimental Part

(Cr,Al)N and (Cr,Mo)N coatings were deposited using an RF dual magnetron sputtering system (NORDIKO 3500–13.56 MHz,

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Table 1. Deposition conditions of the (Cr,Al)N and (Cr,Mo)N coatings.

Coatings	Working pressure	Nitrogen content in the plasma	Cr bias	Al (or Mo) bias	Deposition time
	Pa	%	V	V	min
CrN	0.4	20		–0	90
				–300	
				–500	
			–900	–700	
			–500	–900	
(Cr,Al)N or (Cr,Mo)N			–700		

1250 W). Pure Cr (99.995%), Al (99.999%) and Mo (99.95%) targets (101.6 mm of diameter, 3 mm of thickness) were used. The sputtering rate obtained for 600 eV as the energy of the incident Ar ions was 1.3 for Cr, 1.22 for Al and 0.92 for Mo. In order to modify the Al and Mo contents in the (Cr,Al)N and (Cr,Mo)N layers, respectively, we modified the Cr, Al and Mo target bias. Table 1 gives the deposition conditions of these coatings.

(Cr,Al)N and (Cr,Mo)N coatings have been deposited on silicon (100), $10 \times 10 \times 0.38 \text{ mm}^3$. The ex situ cleaned substrates were fixed on a vertical substrate holder which is also polarized in DC (–1000 V) during etching procedure and on floating potential during the deposition process. The targets/substrates distance was 90 mm, the angle between the two targets is 36 and 18° between the targets and the substrate holder. Prior to the deposition, the vacuum chamber was pumped down to $2 \times 10^{-4} \text{ Pa}$, the substrates and the targets were then in situ etched under argon ions bombardment for 5 min.

The morphology and the thickness of the layers were verified by SEM (JEOL JSM-5900-LV microscope) equipped with an energy dispersive spectroscopy (EDS) microanalysis to determine their composition, the electron energy was 5 keV and the standard deviation of composition quantification was less than 1 at.%. The structure of the coatings was analysed by X-ray diffraction (XRD, SIEMENS D5000 diffractometer, $\theta/2\theta$ configuration, $\text{CoK}\alpha$ radiation). The residual stresses were calculated using the Stoney's equation^[7] after measuring the radius curvature of the silicon coated samples with the Newton's rings method.^[8]

Results and Discussion

Figure 1A shows the chromium, aluminium and nitrogen atomic contents determined by EDS in the (Cr,Al)N films as a function of the Cr and Al target bias (Table 2). First, we observe no presence of C in our coatings and they present up to 2 at.% of oxygen which is negligible for mechanical applications. We observe

that the Al content increases from 0 to 30 at.% with the Al target bias. This result can be explained by the resulting increase of the Al target sputtering rate. However, between –700 and –900 V, we note a weak increase of the Al content from 28 to 30 at.%. According to Ding et al.,^[9] for the same target bias, chromium has a higher sputtering rate than aluminium, which can explain the increase of chromium content compared to the aluminium one for these specific deposition conditions at the highest target bias. We can also note the low increasing of nitrogen content from 28 to 36 at.% with the Al target bias, which indicates that the Al addition is benefit for the enhancement of the CrN stoichiometry. As the maximum Al content obtained was around 30 at.% by increasing the Al target bias, we decided to fix this one and to vary the Cr target bias. It is obvious that it was the main parameter to vary and to get a maximum of 51 at.% of Al which was not expected first. Actually, it was logical that fixing the Cr target bias and varying the Al one would permit us to obtain a maximum of Al in the (Cr,Al)N films but as mentioned before, the sputtering rate of Cr is higher than the Al one which seems to be a decisive parameter. The composition of (Cr,Al)N

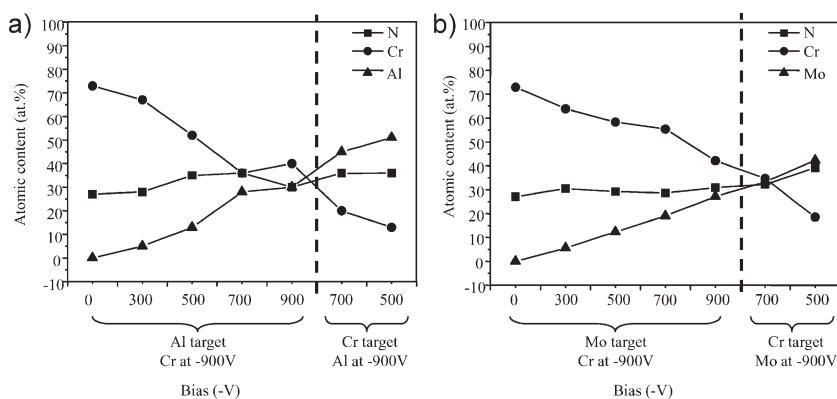


Figure 1. (Cr,Al)N (A) and (Cr,Mo)N (B) composition as a function of Cr and Al or Cr and Mo target, respectively.

Table 2. (Cr,Al)N and (Cr,Mo)N coatings properties.

Coatings	Cr power	Al(or Mo) power	Cr	N	Al(or Mo)	Thickness	Growth rate
	W	W	at. %	at. %	at. %	μm	μm · min ^{−1}
CrN	500	0	73	27	0	1.78	0.019
(Cr,Al)N	500	100	67	28	5	2.1	0.023
	500	250	52	35	13	2.47	0.027
	500	350	36	36	28	2.66	0.029
	500	450	40	30	30	3	0.033
	150	700	20	36	45	2.14	0.023
	250	700	13	36	51	1.94	0.021
(Cr,Mo)N	450	80	64	30	0	0.88	0.009
	450	150	58	29	6	1.08	0.012
	450	250	55	29	12	1.19	0.013
	450	350	42	31	19	1.37	0.015
	150	350	35	32	27	1.07	0.011
	300	300	19	39	33	0.86	0.009

ternary layers is $\text{Cr}_{0.4}\text{Al}_{0.3}\text{N}_{0.3}$ for a bias of -900 V applied on both Cr and Al targets, and $\text{Cr}_{0.13}\text{Al}_{0.51}\text{N}_{0.36}$ for a bias of -900 V applied on Al target and a bias of -500 V applied on the Cr one.

Figure 1B presents the chromium, molybdenum and nitrogen atomic contents determined by EDS in the (Cr,Mo)N films as a function of the Cr and Mo target bias (Table 2). The Mo content varies between 0 and 27 at.% with the Mo target bias which can be explained by the increase of the Mo target sputtering rate. We also note that the N_2 content is about 30 at.% for all the (Cr,Mo)N coatings which indicates that the addition of Mo is not benefit to the enhancement of the CrN stoichiometry. It is noteworthy that for the same Al and Mo target bias, the Al contents in (Cr,Al)N films is always higher than the Mo contents in the (Cr,Mo)N ones. This can be explained by the fact that the sputtering rate of Al is higher than the Mo one.^[10] Finally, as observed in the case of the (Cr,Al)N coatings and for the same reason, we obtained a maximum of 42 at.% of Mo in the (Cr,Mo)N coatings by varying the Cr target bias. The composition of (Cr,Mo)N layers is $\text{Cr}_{0.42}\text{Mo}_{0.27}\text{N}_{0.31}$ for a bias of -900 V applied on both Cr and Mo targets, and $\text{Cr}_{0.19}\text{Mo}_{0.42}\text{N}_{0.39}$ for a bias of -900 V applied on the Mo target and a bias of -500 V for the Cr one.

The (Cr,Al)N coatings thicknesses increase from 2 to 3 μm with the Al target bias (Table 2). This can be explained by the increase of the Al sputtering rate with the bias. When we increased the Cr target bias, the thickness of the layers varied also from 2 to 3 μm. Nevertheless,

the thickness obtained for -700 V on the Al target and -900 V on the Cr target is higher than the one obtained for -900 V on the Al target and -700 V on the Cr target. A same remark was made for -500 and -900 V bias. This confirms that the Cr sputtering rate is higher than the Al one. Similar results have been obtained by Ding et al.^[9]

The evolution of the (Cr,Mo)N coatings' thicknesses is similar (Table 2). Indeed, the thickness increases from 0.88 to 1.37 μm with the Mo target bias which was expected as in the case of the (Cr,Al)N coatings. Besides the same phenomenon about the influence of the Cr sputtering rate at lower bias than Mo was observed but less marked than in the case of the (Cr,Al)N layers. The above results let us concluded that the sputtering rate of Mo is lower than that of Al which is lower than that of Cr, as already proved by Bessot.^[10] We well observed that the (Cr,Al)N coatings' thicknesses exceeded those of the (Cr,Mo)N ones for the same bias.

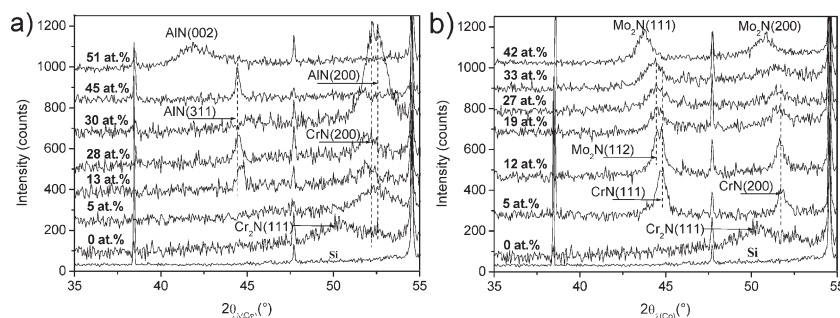


Figure 2. XRD patterns of (Cr,Al)N (A) and (Cr,Mo)N (B) coatings as a function of Al and Mo content, respectively.

The XRD patterns of the (Cr,Al)N coatings deposited with different Al contents are presented in Figure 2A. A broad peak of Cr₂N (111) was observed on the XRD spectrum of the CrN film, which confirms the N/Cr ratio of around 0.4 obtained by the EDS microanalysis (Figure 1A). This broad peak shows that the deposited layer is not well crystallized. By adding 5, 13 and 28 at.% of Al, CrN (200) and AlN (311) diffraction peaks appeared showing that the aluminium addition enhanced the CrN film crystallization. This result is in correlation with other works.^[9,11] At 30 at.% of Al content, a broad peak probably coming from the presence of both CrN (200) and AlN (200) orientation appeared and the layer is then well crystallized. This result was also obtained in several works.^[9,11,12] Moreover, there is a translation of this peak to wide angles showing that (Cr,Al)N films contain compressive stresses, results already observed in a previous study.^[12] According to Ding et al.^[13] this peak is characteristic to the formation of a new system (Cr,Al)N with the (200) orientation. In fact, the EDS analysis shows a (Cr + Al)/N ratio about 2.3 which corresponds to the formation of the compound Cr_{0.4}Al_{0.3}N_{0.3}. However, we cannot confirm this result because even now only the CrN and AlN JCPDS data are available but not those of (Cr,Al)N. This peak completely disappeared from 44 at.% of Al content where only the AlN (311) peak exists and shows that the layer is well crystallized. This last peak disappeared itself at 51 at.% of Al content and is replaced by a broad AlN (002) peak indicating that the deposited layer becomes amorphous.

Figure 2B represents the XRD patterns of the (Cr,Mo)N coatings obtained with different Mo contents. After adding only 5 at.% of Mo, CrN (200) and (111) diffraction peaks appeared showing that the addition of Mo is favourable to the CrN crystallization. These two peaks exist also for 12 at.% of Mo but with another Mo₂N (112) peak which appeared and caused a broad peak composed also of the CrN (111) crystalline orientation. This double peak becomes broad from 19 to 33 at.% of Mo showing that the (Cr,Mo)N deposited films become amorphous while in the case of the (Cr,Al)N coatings, the Al addition improved the CrN crystallization as mentioned above. Besides, the CrN (200) peak completely disappeared at 33 at.% of Mo. The Mo₂N (112) is replaced by a broad (200) peak and another (111) peak at 42 at.% of Mo. In comparison with the (Cr,Al)N coatings where the layers were only composed of

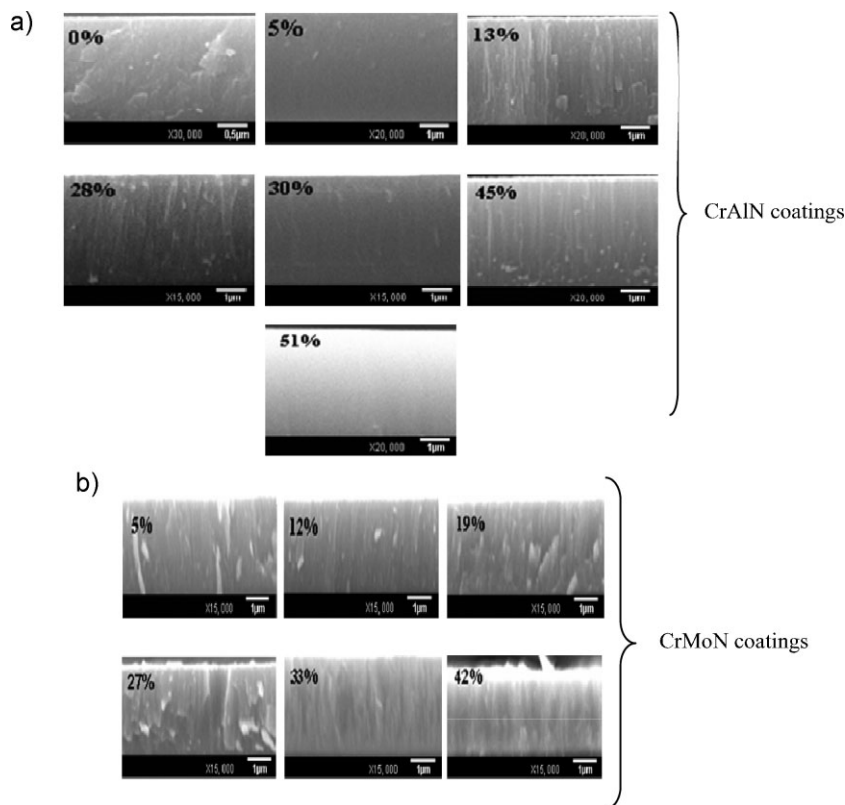


Figure 3. SEM cross-section images of (Cr,Al)N (A) and (Cr,Mo)N (B) coatings for different Al and Mo content, respectively.

aluminium nitride at 44 at.% of Al, at a similar Mo content of 42 at.%, the layers are still crystallized and also only composed of molybdenum nitride. These phase and crystalline orientations transformations were observed by Kim et al.^[4] and Choi et al.^[14]

SEM observations on cross-section (obtained by cutting the coated Si with a diamond tip) of the layers morphology was carried out. Figure 3A shows clearly that the CrN film (0 at.% of Al) is dense and amorphous. By adding Al, the films present a dense (at 5 and 30 at.% of Al) and then a columnar structure clearly visible for 13, 28 and 44 at.% of Al contents. According to the XRD analysis, we noted the appearance of AlN (311) diffraction peak for these films; this morphology can be explained by the formation of the AlN phase. The disappearance of the AlN (311) peak and the presence of the broad peak composed of the CrN (200) and AlN (200) ones could be the cause of the morphological modification of the (Cr,Al)N coatings obtained with 30 at.% of Al which became denser. The morphology of the (Cr,Al)N layers deposited with 51 at.% of Al shows a dense and amorphous structure which is in correlation with the XRD analyses.

Figure 3B shows the SEM observations on cross-section of (Cr,Mo)N-coated silicon substrates. The (Cr,Mo)N coatings

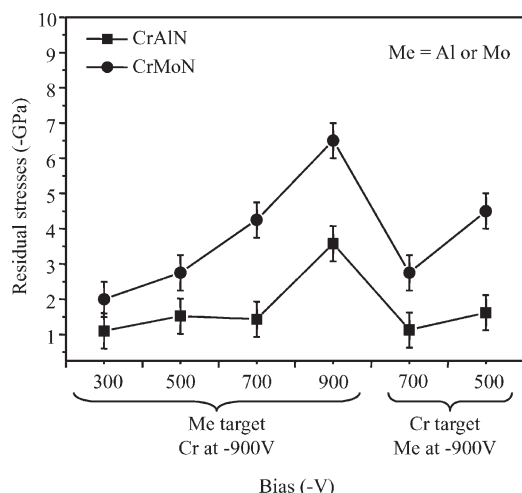


Figure 4. Residual stresses of (Cr,Al)N and (Cr,Mo)N as a function of the target bias (Me = Cr or Mo).

have the same morphology except the ones obtained with 33 and 42 at.% of Mo which show a slight difference. Actually, the (Cr,Mo)N films present a columnar structure for 5, 12, 19 and 27 at.% of Mo. The XRD analyses of these films showed the presence of CrN (200) and (111) diffraction peaks, then one can suppose that the presence of the cubic CrN phase is responsible of this morphology. These two CrN peaks completely disappeared for 33 and 42 at.% of Mo where only the Mo₂N phase is present which could be responsible of the denser morphology of the (Cr,Mo)N layers obtained at the highest Mo contents. We can then suppose that the molybdenum nitride phase is denser than the chromium nitride one.

The residual stresses of the (Cr,Al)N and (Cr,Mo)N coatings as a function of Cr, Al and Mo target bias are presented in Figure 4. The (Cr,Al)N and (Cr,Mo)N deposited films have compressive stresses which vary between –1 and –3.5 GPa and between –2.7 and –6.5 GPa, respectively. Same results have been obtained in previous studies.^[4,14,15] We can see also that the residual stresses of the (Cr,Mo)N films are higher than the (Cr,Al)N ones. This can be explained by the fact that the Mo atomic radius ($R = 201 \text{ \AA}$) is higher than the Al one ($R = 182 \text{ \AA}$), then the substitution of Cr atoms ($R = 185 \text{ \AA}$) by Mo atoms created a main distortion of the CrN lattice than the substitution by Al atoms. It is noteworthy that the residual stresses exhibit the same behaviour for both coatings. They increased with the Al or Mo contents until their highest value for 30 at.% of Al and 27 at.% of Mo, and then they decreased. These maximum values correspond to the formation of the Cr_{0.4}Al_{0.3}N_{0.3} and Cr_{0.42}Mo_{0.27}N_{0.31} systems, which are more stressed than the CrN one because of the implantation of Al and Mo atoms into the CrN system. The same behaviour has been observed by Kim et al.^[4] and Choi et al.^[14] on the other hand, the increase of the residual stresses with the increase

of Al (or Mo) content can be explained by the increase of microstructural defects causing by the substitution of Cr atoms by Al (or Mo) ones. Besides, when the Cr target bias decreased from –900 to –700 V (or –500 V), the energy of the Cr incident atoms on the substrate is smaller than those when we applied –900 V which can explain the decrease of the residual stresses by the creation of defects like a columnar structure and as a consequence, the layers are less dense (Figure 3). So, two phenomena could explain the variation of the residual stresses; the substitution of Cr atoms by Al or Mo ones and the energy of the incident species or atoms during the sputtering process.

Conclusion

The effect of the addition of Al or Mo on the physicochemical, structural and morphological properties and the residual stresses of the Cr–N system was studied. The above results allow us to conclude as follows:

- The addition of Al enhances the stoichiometry of the Cr–N system which is confirmed by the increase in N₂ content from 28 to 36 at.% with the Al target bias. In contrast, the N₂ content was constant and equal to 30 at.% for all (Cr,Mo)N layers which indicates that the addition of Mo is not benefit to enhance the Cr–N stoichiometry.
- XRD analyses showed that the addition of Al improves the crystallization of the Cr–N system. For (Cr,Mo)N coatings, we observed that the addition of Mo is less benefit to the structural improvement of the Cr–N system in comparison with the Al one.
- The SEM cross-section observations confirmed the results obtained by the XRD analyses. Indeed a change from amorphous to columnar structure was obtained when the Al content increased for the (Cr,Al)N layers. In contrast, a slight change for the (Cr,Mo)N coatings' morphology was observed for the highest Mo contents.
- Both (Cr,Al)N and (Cr,Mo)N coatings showed compressive residual stresses which exhibited a similar behaviour as a function of the applied target bias. The main phenomenon that could explain the increase of the residual stresses when we varied the Al or Mo target bias is the substitution of Cr atoms by Al or Mo ones but a second phenomenon like the energy of the incident species or atoms during the sputtering process should be took into account to explain the decrease of the residual stresses when we varied the Cr target bias.

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